

DIVISION S-3—SOIL BIOLOGY & BIOCHEMISTRY

Temporal Variability of Soil Carbon Dioxide Flux: Effect of Sampling Frequency on Cumulative Carbon Loss Estimation

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ABSTRACT

It is well known that soil CO₂ flux can exhibit pronounced day-to-day variations; however, measurements of soil CO₂ flux with soil chambers typically are done only at discrete points in time. This study evaluated the impact of sampling frequency on the precision of cumulative CO₂ flux estimates calculated from field measurements. Automated chambers were deployed at two sites in a no-till corn/soybean field and operated in open system mode to measure soil CO₂ fluxes every hour from 4 March 2000 through 6 June 2000. Sampling frequency effects on cumulative CO₂-C flux estimation were assessed with a jackknife technique whereby the populations of measured hourly fluxes were numerically sampled at regular time intervals ranging from 1 d to 20 d, and the resulting sets of jackknife fluxes were used to calculate estimates of cumulative CO₂-C flux. We observed that as sampling interval increased from 1 d to 12 d, the variance associated with cumulative flux estimates increased. However, at sampling intervals of 12 to 20 d, variances were relatively constant. Sampling once every 3 d, estimates of cumulative C loss were within $\pm 20\%$ of the expected value at both sites. As the time interval between sampling was increased, the potential deviation in estimated cumulative CO₂ flux increased such that sampling once every 20 d yielded potential estimates within $+60\%$ and -40% of the actual cumulative CO₂ flux. A stratified sampling scheme around rainfall events was also evaluated and was found to provide more precise estimates at lower sampling intensities. These results should aid investigators to develop sampling designs to minimize the effects of temporal variability on cumulative CO₂-C estimation.

CONCERN ABOUT GLOBAL climate change has fostered a renewed interest in increasing soil C sequestration in agricultural systems as a strategy to offset atmospheric CO₂ increases. This has resulted in a greater effort to understand the factors affecting soil C storage, as well as to assess soil C budgets (Lal et al., 1995). Carbon dioxide flux from soil to the atmosphere is the primary mechanism of C loss from soils and is a major component of terrestrial C budgets. Quantification of C losses relative to inputs may be a valuable technique for estimating the rate of change of the soil C pools and for evaluating the impact of management practices on C sequestration in agricultural systems (Buyanovsky et al., 1985; Curtin et al., 2000; Duiker and Lal, 2000; Paus-tian et al., 1997).

Estimation of cumulative CO₂ flux from the soil surface during the time periods required to evaluate agricultural management practices remains problematic.

High temporal and spatial variability may often mask differences in CO₂ flux arising from management changes (Duiker and Lal, 2000; Hutchinson et al., 2000). The spatial variability of soil CO₂ flux has been characterized in several studies (Davidson et al., 2002; Rayment and Jarvis, 2000; Rochette et al., 1991), and coefficients of variation in the range of 25 to 85% have been reported. With such information, sample number requirements to achieve an estimate with a given precision can be calculated with standard techniques (Jensen et al., 1996; Rochette et al., 1991; Snedecor and Cochran, 1967). The temporal variability of soil CO₂ flux has also been characterized. Seasonal changes in CO₂ flux have been reported to follow seasonal temperature trends (Anderson, 1973; Buyanovsky et al., 1985; Franzluebbers et al., 2002; Raich and Tufekcioglu, 2000; Rochette et al., 1991). Across shorter time scales, abrupt changes in soil CO₂ flux can occur in response to rainfall events (Curtin et al., 2000; Duiker and Lal, 2000; Jensen et al., 1996; Rochette et al., 1991).

Whereas the temporal dynamics of CO₂ flux and the factors controlling these dynamics are fairly well known, application of this knowledge to guide sampling through time has been generally overlooked. Franzluebbers et al. (2002) recently observed that soil respiration was strongly autocorrelated up to a lag of 10 d, and more weakly correlated at longer lags. These workers recommended that a 10-d sampling interval be used to assess environmental controls on soil respiration. Despite the recommendations of sampling frequency that appear in the literature, the efficacy of such recommendations with regard to the precision of estimates obtained is not available.

Use of point-in-time measurements of CO₂ flux to evaluate effects of soil management on C sequestration in agricultural systems requires better understanding of the consequences of a given temporal sampling protocol with regard to the precision of the estimate obtained. Thus, the objectives of this study were to determine the effect of sampling frequency on cumulative CO₂-C flux estimation calculated from short-term CO₂ flux measurements obtained with automated open-system dynamic chambers, and to evaluate a sampling scheme, stratified around rainfall events, with regard to improvement of CO₂-C flux estimation.

MATERIALS AND METHODS

Site Description and Soil Characteristics

A field study was conducted in an established no-till corn and soybean management system in Boone County, Iowa.

Abbreviations: DOY, day of year; IRGA, infrared gas analyzer.

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Table 1. Soil properties at the two study sites. Soil properties were determined on soil cores collected from the CO₂ flux chambers at the end of the experiment (0–25 cm depth). Four cores were collected from each chamber and bulked. Values in parentheses are standard deviations of two chambers at each site.

Soil	Bulk density Mg m ⁻³	pH	Organic N	Organic C	Sand	Silt	Clay
					g kg ⁻¹		
Clarion	1.37 (0.030)	6.0 (0.4)	1.2 (0.006)	12.9 (0.10)	588 (32)	247 (28)	165 (18)
Canisteo	1.19 (0.003)	6.8 (0.2)	2.9 (0.030)	36.0 (0.55)	405 (32)	342 (17)	253 (24)

Beginning in March 2000, instrumentation for CO₂ flux measurements was installed at two sites within the field, each having different soil types and landscape positions. One site was an eroded Clarion sandy loam soil (fine-loamy, mixed, superactive, mesic Typic Hapludolls) on an upper backslope and the other site was a Canisteo clay loam soil (fine-loamy, mixed, superactive, calcareous, mesic Typic Endoaquolls) on a footslope. The sites were approximately 91 m apart. Both soils had a 10-yr history of corn and soybean rotation under no-tillage management. Soybean had been grown in the field in 1999 and the corn planting in 2000 was delayed until after the measurements were completed at the two sites.

Surface soil (0–25 cm) within each of the four CO₂ flux chambers was sampled after the measurement period. Four soil cores (3.35-cm diam.) were collected from each chamber and bulked. In the laboratory, samples were weighed and sieved (2 mm). Subsamples were collected for water content determination by oven drying at 105°C, and the remaining soil was air dried. Air-dried samples were ground with a roller mill for organic C and N determination by dry combustion with a Carlo-Erba NA 1500 CHN elemental analyzer (Haakes Buchler Instruments, Paterson, NJ) after removal of carbonates (Nelson and Sommers, 1996). The pH was measured in 1:1 distilled water-to-soil slurries. Bulk density was computed from the soil sample weights (corrected for water content) and the known core volume. Soil texture analyses were performed by Midwest Laboratories, Inc. (Omaha, NE). Physical and chemical properties of the two soils are shown in Table 1.

Field Instrumentation and Measurements

At each site, two CO₂ flux chambers, similar in design to those of Ambus and Robertson (1998), were installed. The chambers were 0.60- by 0.60- by 0.30-m-tall stainless steel open-ended boxes pressed into the soil approximately 0.05 m. The top of each steel box was fit with a wooden framework that supported a sliding cover. The covers were supported by casters riding on steel tracks attached to the sides of the chambers. Linear actuators driven by gear motors attached to the frames opened and closed the covers at hourly intervals. Carbon dioxide flux was measured every hour from 4 Mar. 2000 [Day of Year (DOY) 64] through 6 June 2000 (DOY 158) by sliding the cover over the chamber top to close the chamber and allow CO₂ to accumulate in the chamber headspace. Carbon dioxide was measured during a 10-min period by pumping the chamber headspace gas through an infrared gas analyzer (IRGA) (LI-800 GasHound; LiCor, Lincoln, NE)¹ and out to the atmosphere. The gas flow rate through the chambers was approximately 0.0108 L s⁻¹. A vent port (11 mm in diam.) in each chamber allowed pressure equilibration within the chambers during pump operation. There were no significant pressure differentials (>0.1 Pa) between the interior and exterior of the chambers during operation, as mea-

sured with a digital micromanometer (Infiltex model DM1, Infiltex, Waynesboro, VA).

Headspace CO₂ concentrations were determined at 1-min intervals in each chamber, and after 10 min, the chambers were reopened. A small fan was located in each chamber to mix the air (1.9 L s⁻¹) during the CO₂ flux measurements. The headspace CO₂ concentration vs. time data were typically curvilinear, indicating that CO₂ flux was limited by a reduction in the diffusion rate caused by increasing headspace CO₂ concentrations during the time the chambers were closed. To correct for this effect, flux rates were calculated from the CO₂ flux data using the algorithm of Hutchinson and Mosier (1981). Because chambers were operating in an open-system mode (headspace gas from the vented chambers was pumped through the IRGA and out to the atmosphere), corrections were made for the mass of CO₂ entering the chamber from the vent port as well as the mass of CO₂ removed from the chamber by the IRGA pump. Initial CO₂ concentrations were determined from an ambient CO₂ concentration measurement obtained immediately before the chambers were closed. Because of the low gas pumping rate (≈ 0.0108 L s⁻¹) relative to the chamber headspace volume (≈ 90 L), these corrections accounted for <1% of the measured headspace CO₂ concentration at each time point.

Each chamber was instrumented with thermocouples to measure air and soil temperature within each chamber while the chambers were closed for CO₂ flux measurements. Soil temperature in each chamber was measured at the surface with two thermocouples placed just under the residue layer, and with two thermocouples inserted 0.05 m below the soil surface. Air temperature in each chamber was measured with two thermocouples suspended ≈ 0.08 m above the soil surface. The air temperature thermocouples were not exposed to direct sunlight when the chambers were closed. Two soil water probes (Delta-T Theta Probes, Dynamax, Houston, TX) were installed in the surface soil (0.00–0.06 m) of each chamber. Soil water content probes were calibrated at each site and the slight temperature effect on probe response (≈ 0.005 kg kg⁻¹ °C⁻¹) was corrected with an empirically derived equation. Temperature and soil water content measurements were made at hourly intervals during the time when the chambers were closed, and average values during each hourly CO₂ flux measurement period are reported. A tipping bucket rain gauge (Campbell Scientific, Logan, UT) was installed at each site, and hourly cumulative rainfall was logged only during periods when the chambers were open to the atmosphere. Power to each station was provided by two 12-V deep-cycle batteries, connected in parallel, and supplemented with solar cells. Each site was also instrumented with a data logger (CR21X, Campbell Scientific) which controlled the chamber automation and collected the hourly data.

Evaluation of Sample Frequency Effects

Sampling frequency effects on cumulative CO₂–C flux estimation were assessed with a jackknife technique (Efron and Gong, 1983). For this analysis, the population of hourly fluxes was numerically sampled at regular time intervals. Sampling

¹ Reference to a trade or company name is for specific information only and does not imply approval or recommendation of the company or product by the USDA to the exclusion of others that may be suitable.

time intervals ranged from 1 to 20 d. The resulting sets of fluxes generated by each jackknife sampling were then used to calculate estimates of cumulative CO_2 -C flux by linear interpolation and numerical integration. These cumulative flux estimates were compared with the overall cumulative flux obtained from all the hourly fluxes for each chamber. From this comparison, estimates of precision as a function of sampling intensity were obtained. In addition to the regular sampling schemes described above, a stratified sampling scheme was also evaluated by integrating hourly fluxes obtained 1 and 3 d following days when rainfall occurred. This sampling scheme was applied with four different rainfall thresholds (1, 2, 4, and 5 mm). To minimize biases induced by diurnal variability in CO_2 flux, jackknife estimates from the regular and stratified sampling scheme were only obtained by sampling the morning and afternoon flux estimates when diurnal bias (with respect to the daily average) was at a minimum (Parkin and Kaspar, 2003). These times corresponded to 0900 and 1900 h for the chambers at the Clarion site, and 0800 and 1900 h for chambers at the Canisteo site. The number of jackknife samplings was dependant upon the precise sampling frequency that was being evaluated, and ranged from 4 to 40. Time series analysis (Statistix, Analytical Software, Tallahassee, FL) was performed on the data to assess the degree of temporal correlation between CO_2 flux and rainfall.

RESULTS

Rainfall, soil water content, and temperature were measured at hourly intervals from 4 Mar. through 6 June 2000 (Fig. 1). During this 95-d period, measurable rainfall (>0.25 mm) occurred on 26 different days. Twelve of the rainfall events resulted in daily rainfall totals <1 mm, and only 4 d had total daily rainfall exceeding 5 mm (Fig. 1A). Soil water content was different at the two sites, with the coarser-textured Clarion soil consistently drier than the finer-textured Canisteo soil. Water content at both sites responded to rainfall events, but the Clarion site exhibited more rapid drying during the periods following rainfall events. Mean daily air temperature increased during the study period from an average of 8.6°C during the first 10 d to an average of 20.8°C during the final 10 d (Fig. 1B). The seasonal increase in mean temperature was overshadowed by the diurnal air temperature fluctuations, which averaged 21°C (difference between daily maximum and minimum). Soil temperature (surface soil and 5-cm depth) followed the same seasonal trend as air temperature; however, diurnal temperature fluctuations were lower than air temperature fluctuations (data not shown). Average diurnal differences between maximum and minimum temperatures were 7.7 and 5.2°C for surface and soil temperatures, respectively.

Carbon dioxide fluxes measured at hourly intervals also exhibited diurnal variability (Fig. 1C–1F). The amplitudes of the diurnal fluctuations varied substantially during the study period, with the highest diurnal responses occurring after rainfall, and the lowest diurnal responses during periods of lower soil water content. There was no consistent relationship between rainfall amount and the magnitude of the CO_2 flux response. For example, Clarion chamber 1 CO_2 flux exhibited a nearly five-fold increase (from $0.054 \text{ g C m}^{-2} \text{ h}^{-1}$ to

$0.196 \text{ g C m}^{-2} \text{ h}^{-1}$) following a small rainfall event (0.25 mm) on DOY 68. Yet, the same chamber showed no response to a rainfall of similar magnitude on DOY 92 and only a 50% increase in CO_2 flux was observed following a 0.78 -mm rain on DOY 84. Also, there appeared to be a differential response to rainfall between the two sites. The CO_2 flux response to rainfall at the Clarion site was larger than at the Canisteo site. This is evident near the latter part of the measurement period (DOY 140–159), when several rainfall events triggered large CO_2 responses at the Clarion site, but at the Canisteo site, the CO_2 response was less pronounced. It is likely that the interactions between temperature, rainfall, water content, and available C, as influenced by wetting and drying, influenced CO_2 flux.

A jackknife procedure was used to determine the influence of sampling frequency on cumulative CO_2 flux estimation. In a previous study (Parkin and Kaspar, 2003), we determined that diurnal biases were minimal with fluxes determined at 0900 and 1900 h for the Clarion site and at 0800 and 1900 h for the Canisteo (Table 2). Integration of all the hourly fluxes across the study period resulted in cumulative C flux estimates of 161.8 and 153.6 g C m^{-2} for Clarion Chambers 1 and 2, respectively, and 123.8 and 122.3 g C m^{-2} for Canisteo Chambers 3 and 4, respectively (Table 2). These values serve as best estimates of the cumulative CO_2 -C loss for each chamber. The cumulative CO_2 flux estimates obtained with only the morning or afternoon measurements were similar to the cumulative C fluxes calculated with all the hourly values. The bias associated with use of the morning fluxes ranged from 5.2 to -0.65% , while the bias associated with the afternoon fluxes ranged from 1.64 to -4.03% .

In the implementation of the jackknife procedure, we selected subsets of hourly flux measurements at regular intervals throughout the sample period and computed cumulative CO_2 -C flux estimates from each run. The time interval between samples was varied from 1 to 20 d. For each jackknife sample, a cumulative CO_2 -C flux was calculated (Fig. 2). Also shown in Fig. 2 are the cumulative flux estimates for each chamber based on all the hourly estimates (horizontal lines). As the interval between sampling days increased, the spread of potential realizations of cumulative C flux also increased. At the Clarion site, the spread of potential cumulative CO_2 -C fluxes was larger than at the Canisteo site. However, this effect is because of the fact that cumulative CO_2 flux was greater at the Clarion site than at the Canisteo site.

The influence of sample interval on relative spreads of potential cumulative CO_2 -C flux estimates for the two sites are obtained by computing the percentage deviation of each jackknife estimate from the best estimate obtained from all the hourly flux measurements of each chamber (Fig. 3). This representation yields estimates of the potential errors associated with cumulative flux estimation for different sampling intensities. At relatively frequent sampling intensities (i.e., once every 3 d) estimates of cumulative C loss are within $\pm 20\%$ of the expected value at both sites. As the time

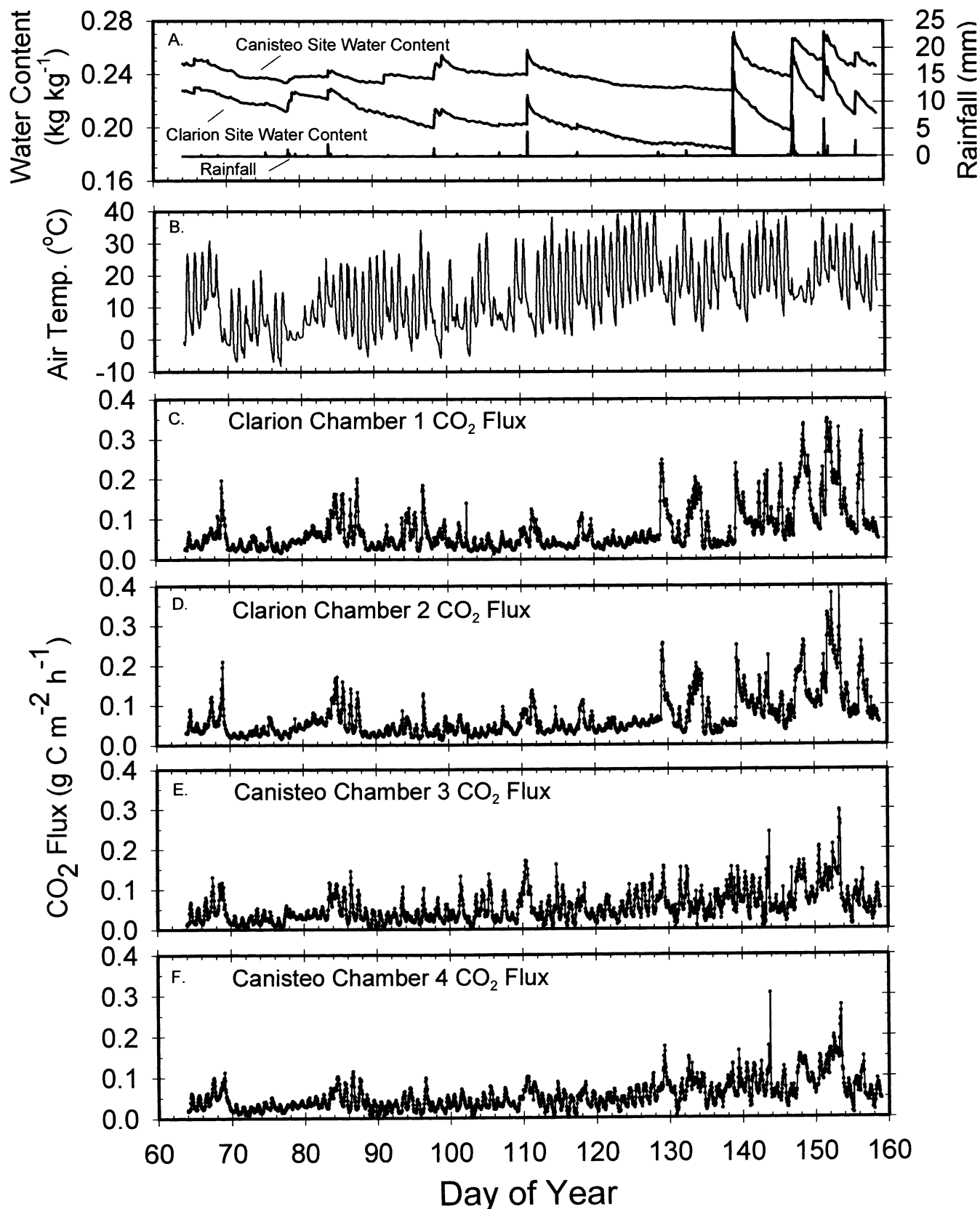


Fig. 1. Hourly measurements of soil water content, rainfall, air temperature, and CO_2 flux. Soil water content data is average for each site. Carbon dioxide fluxes for each individual chamber are presented. Two chambers were located on the Clarion site and two chambers were located at the Canisteo site.

Table 2. Accuracy of CO₂-C estimation based on sampling at times of day when average unbiased daily CO₂ flux occurs. Cumulative CO₂-C fluxes for each chamber were determined using all 24 of the hourly flux measurements each day of the study period, and using only a single hourly flux measured in the morning or in the afternoon of each day. For the Clarion chambers, flux measurements at 0900 h and 1900 h were used. For the Canisteo chambers, flux measurements at 0800 h and 1900 h were used.

Chamber	All hours	Morning	Afternoon	Morning	Afternoon
	g CO ₂ -C m ⁻²			% Bias	
Clarion-1	161.8	166.4	158.3	2.84	-2.16
Clarion-2	153.6	161.6	147.4	5.20	-4.03
Canisteo-1	123.8	123.0	121.0	-0.65	-2.26
Canisteo-2	122.3	125.2	124.3	2.37	1.64

interval between sampling increases, the potential deviation in estimated cumulative CO₂ flux increases, such that sampling once every 20 d yields potential estimates within approximately +60% and -40% of the actual cumulative CO₂ flux.

To quantify this variability, we computed variances of the percentage deviations (Fig. 4). The influence of sampling interval on the variances associated with estimated cumulative CO₂ flux were similar for both sites. Variances increased sharply as sampling interval increased up to a sampling interval of 12 d. At sampling intervals longer than 12 d, the variance associated with estimates of cumulative CO₂-C flux was nearly constant.

Presented in Fig. 5 are the probabilities associated with obtaining estimates of cumulative CO₂-C loss within a given percentage of the actual CO₂-C flux. To discern how temporal variability impacts estimation of cumulative C flux estimates at different sampling frequencies, we calculated the estimation probabilities across a range of precisions. For each site we computed the relationship between sample interval and probability at four precision levels; 10, 20, 30, and 50%. This information allows for assessment of how well cumulative CO₂ flux is estimated for different sampling intensities across a range of probability levels. For example, at the Canisteo site, to obtain an estimate of the cumulative CO₂-C flux within $\pm 10\%$ of the actual flux with a >90% probability, one must perform a CO₂ flux measurement

every 3 d. It is evident from Fig. 5 that for each estimation precision, the probability of obtaining an estimate of cumulative CO₂ flux at a given precision decreases with increasing sampling frequency, and that the rate of decrease is a function of the desired precision. Thus, if the desired precision is only 50%, then little is gained by sampling every day as compared with sampling every 20 d.

One of primary factors controlling the temporal variability of soil CO₂ flux, and hence, impacting the sampling precision is rainfall. If, in a regular sampling scheme, the interval between successive sampling events is too large, then the CO₂ flux response to rainfall may be inadequately characterized. Potential problems include underestimation of cumulative CO₂ flux if significant rainfall events are missed, or overestimation of cumulative CO₂ flux if flux measurements performed following rainfall events are weighted too heavily because an unrepresentative number of dry periods are included in the data set. To account for these potential problems, we evaluated a stratified sampling scheme whereby sampling was dictated by rainfall events. Time series analysis indicated a significant cross correlation between rainfall and CO₂ flux on the day the rain occurred and one day

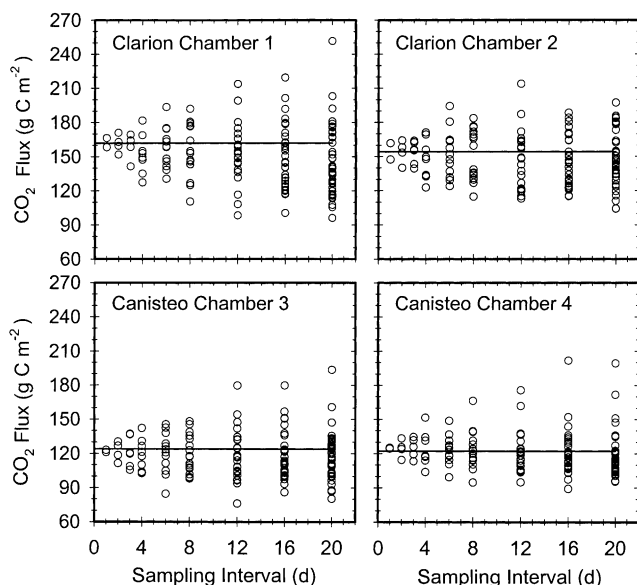


Fig. 2. Influence of time between measurements on estimated cumulative CO₂-C flux for each chamber.

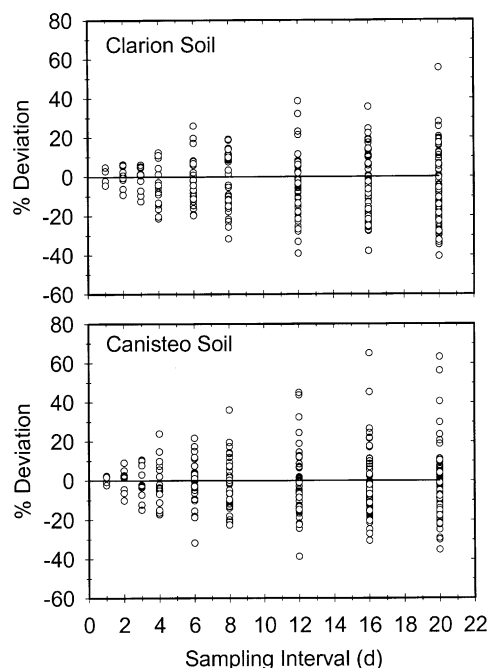


Fig. 3. Influence of sampling interval on deviation of estimated cumulative flux from the best estimate obtained from all the hourly fluxes. Duplicate chambers at each site were combined.

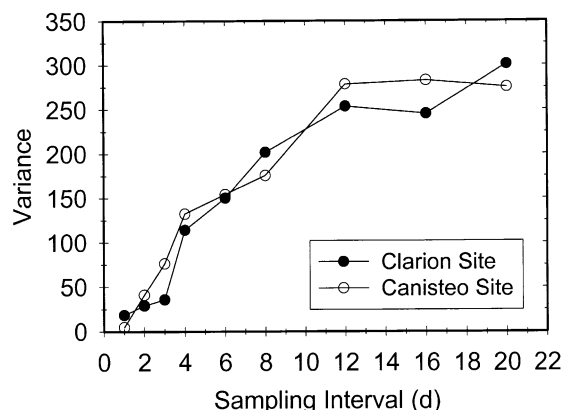


Fig. 4. Variances associated with the spread of percentage deviations observed at different sampling intervals.

following rain (Fig. 6). Three days following rain, the correlation coefficients were similar to prerainfall values and not significant. The periodicity exhibited by the rainfall- CO_2 flux cross correlation at positive lags is because of the temporal rainfall pattern during the study period. Autocorrelograms of rainfall showed similar periodicity with peaks in autocorrelation coefficients occurring at 4-d intervals (data not shown). The cross correlation patterns of rainfall and CO_2 flux were similar at the two sites. With this information, we devised a sampling scheme whereby the population of hourly fluxes was sampled both the day following rainfall and 3 d following rainfall. This sampling scheme was applied with four different thresholds for rainfall (1, 2, 4, and 5 mm). The percentage deviation of the cumulative CO_2 -C fluxes calculated with this stratified sampling scheme were calculated as was done with the regular sampling scheme described previously. Deviations of the estimates of cumulative CO_2 flux from the actual cumulative CO_2 -C loss were calculated (Fig. 7). The range of potential estimates of cumulative CO_2 -C flux when sampling was performed following days when rainfall exceeded 1 or 2 mm was relatively small compared with the spread of potential estimates obtained sampling after days with rainfalls that exceeded 4 or 5 mm. Sampling after 1-, 2-, 4-, and 5-mm rainfall resulted

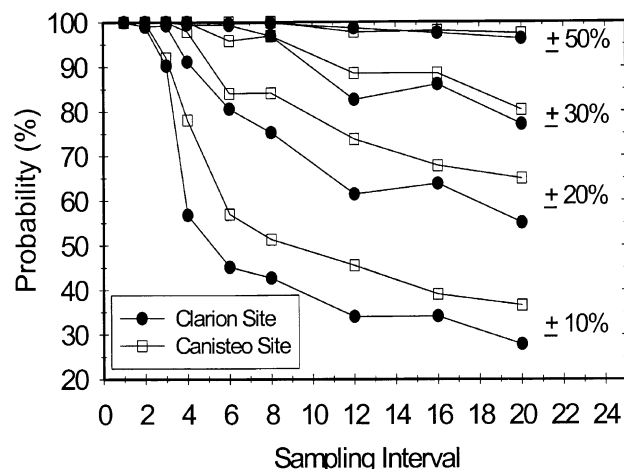


Fig. 5. Probabilities of obtaining estimates of cumulative CO_2 -C flux at a given precision as a function of sampling intervals.

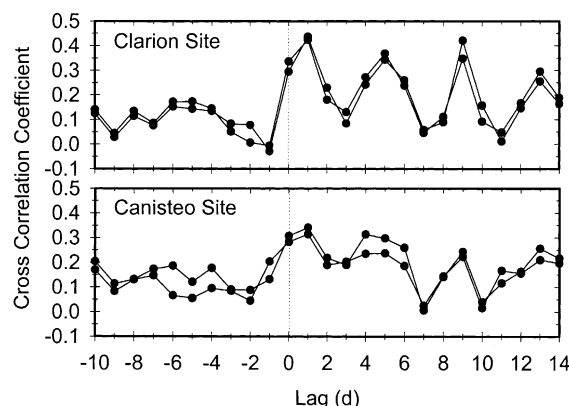


Fig. 6. Time series cross correlation of rainfall and average daily CO_2 flux. Both chambers from each site are represented.

in 23, 21, 11, and 8 sampling times, respectively, during the 95-d period. The resulting average sampling intensities associated with these sampling schemes is also presented in Fig. 7. Errors associated with sampling after 1- and 2-mm rainfall events were within $\pm 11\%$ and were less than sampling at the regular intervals of 4 d (errors $\approx \pm 20\%$, see Fig. 3). Sampling after rainfall events exceeding 4 or 5 mm only slightly improved estimation efficiency over regular sampling at the same intensity. The range of estimated percentage deviations was +45 to -14% for the stratified sampling scheme triggered by rainfall events ≥ 5 mm, while at similar sampling intensity ($n = 12$), the regular sampling scheme yielded percentage deviations in the range of $\pm 45\%$.

DISCUSSION

Temporal variability has been recognized as a confounding factor in the estimation of cumulative CO_2 -C loss from chamber-based CO_2 flux measurements. Despite the potential importance of this issue, guidelines for sampling frequency associated with CO_2 flux measurements are not well defined. Typically, measurements are made on a regular schedule (weekly, biweekly, monthly), however, little information exists concerning

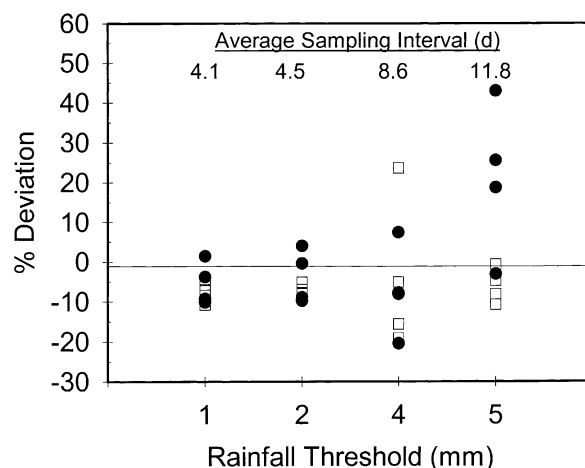


Fig. 7. Deviation of estimated cumulative CO_2 -C flux determined by sampling after days receiving rainfalls of different intensities. Squares are results from the Canisteo site, circles are from the Clarion site.

the adequacy of such sampling regimes with regard to CO₂ cumulative flux estimation. In a direct comparison of CO₂ flux measured manually at weekly intervals and CO₂ flux measured hourly with automated chambers during a 58-d period, Savage and Davidson (2003) found good agreement between with calculated cumulative CO₂-C loss estimated using the two sampling frequencies (0.26 kg C m⁻² vs. 0.27 kg C m⁻²). However, these investigators speculated that the closeness of this comparison may have been fortuitous, because of the canceling effect of the extreme high and low fluxes measured by the manual method at weekly intervals. In a recent study, Franzluebbers et al. (2002) applied geostatistics to characterize the temporal variability of soil respiration. It was observed that variance of soil respiration showed a strong temporal dependence during lags of up to 30 d; however, temporal dependence was stronger during lags of 1 to 10 d. Our study yielded similar results, namely, the variance associated with estimates of cumulative flux increased with increasing time between measurement times up to 12 d. From 12- to 20-d lag intervals, variability increased only slightly. On the basis of the temporal structure of the variability associated with CO₂ flux and other soil variables, Franzluebbers et al. (2002) recommended a sampling interval of ≈10 d if resources are limited. The relatively stable variances we observed at sampling intervals ≥12 d indicate that little gain in estimation precision is achieved in sampling every 12 d compared with sampling every 20 d.

It is widely recognized that rainfall events can influence the temporal variability of soil CO₂ flux, and thus influence the relationship between sampling frequency and cumulative CO₂-C loss. Duiker and Lal (2000) were unable to reconcile their estimates of cumulative CO₂ loss against changes in the soil organic C pool in a carbon budget study of a no-till system. They speculated that temporal variability was a potential reason for this inconsistency and that their biweekly sampling scheme failed to capture the peaks and dips associated with transient fluxes triggered by rainfall events. These workers recommended more frequent measurement, especially around rainfall events. This recommendation is similar to that made by Rochette et al. (1991), who concluded that weekly CO₂ flux measurements may lead to errors in CO₂ flux estimation due to inadequate characterization of the response to rainfall. Their recommendation was that CO₂ flux be measured 1, 3, and 5 d following rainfall events.

Whereas suggestions in the literature exist regarding sampling frequency, there is little direct evidence concerning the efficacy of adoption of such recommendations on the precision of resulting CO₂ flux estimates. Results of our study indicate that sampling 1 and 3 d following days when rainfall exceeded 1 or 2 mm yielded estimates of cumulative C loss within ±11% of the actual value (determined from the 2280 hourly measurements collected during the study period). Variability associated with cumulative CO₂-C loss estimates obtained from sampling at regular intervals of approximately the same frequency (4 d) was twice as high (±21%). Sampling only after large rainfalls (>4 mm)

did not result in substantial improvement in estimation as compared with regular sampling at the same frequency.

Specific recommendations regarding the frequency of regular sampling must consider not only the sampling frequency and variance relationship, but also must consider the objectives of the particular study as well as the resources available to the investigator. Because of this, we do not make specific recommendations for temporal sampling of CO₂ flux. However, the information provided in this study may aid researchers in making informed decisions to maximize available resources. While we observed similar variance structures with the two different soils of this study, the generality of our results needs to be demonstrated by investigations on other soils. Also, it remains to be determined what extent the year-to-year variation in rainfall pattern has on temporal variance structure of soil CO₂ flux, and whether relationships can be developed between rainfall pattern and sampling efficacy. Our current research is directed at addressing these questions.

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REFERENCES

- Ambus, P., and G.P. Robertson. 1998. Automated near-continuous measurement of carbon dioxide and nitrous oxide fluxes from soil. *Soil Sci. Soc. Am. J.* 62:394–400.
- Anderson, J.M. 1973. Carbon dioxide evolution from two temperate, deciduous woodland soils. *J. Appl. Ecol.* 10:361–378.
- Buyanovsky, G.A., C.L. Kucera, and G.H. Wagner. 1985. Comparative carbon balance in natural and agricultural ecosystems. *Bull. Ecol. Soc. Am.* 66:149–150.
- Curtin, D., H. Want, F. Selles, B.G. McConkey, and C.A. Campbell. 2000. Tillage effects on carbon fluxes in continuous wheat and fallow-wheat rotations. *Soil Sci. Soc. Am. J.* 64:2080–2086.
- Davidson, E.A., K. Savage, L.V. Verchot, and R. Navarro. 2002. Minimizing artifacts and biases in chamber-based measurements of soil respiration. *Agric. For. Meteorol.* 113:21–37.
- Duiker, S.W., and R. Lal. 2000. Carbon budget study using CO₂ flux measurements from a no till system in central Ohio. *Soil Tillage Res.* 54:21–30.
- Efron, B., and G. Gong. 1983. A leisurely look at the bootstrap, the jackknife, and cross-validation. *Am. Stat.* 37:36–48.
- Franzluebbers, K., A.J. Franzluebbers, and M.D. Jawson. 2002. Environmental controls on soil and whole-ecosystem respiration from a tallgrass prairie. *Soil Sci. Soc. Am. J.* 66:254–262.
- Hutchinson, G.L., G.P. Livingston, R.W. Healy, and R.G. Striegl. 2000. Chamber measurement of surface-atmosphere trace gas exchange: Numerical evaluation of dependence on soil, interfacial layer, and source/sink properties. *J. Geophys. Res.* 105:8865–8875.
- Hutchinson, G.L., and A.R. Mosier. 1981. Improved soil cover method for field measurement of nitrous oxide fluxes. *Soil Sci. Soc. Am. J.* 45:311–316.
- Jensen, L.S., T. Mueller, K.R. Tate, D.J. Ross, J. Magid, and N.E. Nielsen. 1996. Soil surface CO₂ flux as an index of soil respiration in situ: A comparison of two chamber methods. *Soil Biol. Biochem.* 28:1297–1306.
- Lal, R., J. Kimble, and B.A. Stewart. 1995. World soils as a source or sink for radiatively-active gases. p. 1–7. *In* R. Lal et al. (ed.) *Soil management and greenhouse effect, advances in soil science*. CRC press, Boca Raton, FL.
- Nelson, D.W., and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. p. 961–1010. *In* D.L. Sparks et al. (ed.) *Methods of soil analysis. Part 3. SSSA Book Ser. No. 5. SSSA and ASA*, Madison, WI.

- Parkin, T.B., and T.C. Kaspar. 2003. Temperature controls on diurnal carbon dioxide flux: Implications for estimating soil carbon loss. *Soil Sci. Soc. Am. J.* 67:1763–1772.
- Paustian, K., H.P. Collins, and E.A. Paul. 1997. Management controls on soil carbon. p. 51–72. *In* E.A. Paul et al. (ed.) *Soil organic matter in temperate agroecosystems*. CRC Press, Boca Raton, FL.
- Raich, J.W., and A. Tufekcioglu. 2000. Vegetation and soil respiration: Correlations and controls. *Biogeochemistry* 48:71–90.
- Rayment, M.B., and P.G. Jarvis. 2000. Temporal and spatial variation of soil CO₂ efflux in a Canadian boreal forest. *Soil Biol. Biochem.* 32:35–45.
- Rochette, P., R.L. Desjardins, and E. Pattey. 1991. Spatial and temporal variability of soil respiration in agricultural fields. *Can. J. Soil Sci.* 71:189–196.
- Savage, K., and E.A. Davidson. 2003. A comparison of manual and automated systems for soil CO₂ flux measurements: Trade-offs between spatial and temporal resolution. *J. Exp. Bot.* 54:891–899.
- Snedecor, G.W., and W.G. Cochran. 1967. *Statistical methods*. The Iowa State University Press, Ames.